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<b>(21) International Application Number:</b> PCT/GB96/01244 <b>(22) International Filing Date:</b> 23 May 1996 (23.05.96)  <b>(30) Priority Data:</b> 9510418.8 23 May 1995 (23.05.95) GB 9607395.2 10 April 1996 (10.04.96) GB  <b>(71) Applicant (for all designated States except AT BE CH DE DK ES FI FR GB GR IE IT LU MC NL PT SE US):</b> KABUSHIKI KAISHA KOBE SEIKO SHO also known as KOBE STEEL, LTD. [JP/JP]; 3-18, 1-chome, Wakinohama-cho, Chuo-hu, Kobe 651 (JP).  <b>(71) Applicant (for AT BE CH DE DK ES FI FR GB GR IE IT LU MC NL PT SE only):</b> KOBE STEEL EUROPE LTD. [GB/GB]; Research Laboratory, 10 Nugent Road, Surrey Research Park, Guildford, Surrey GU2 5AF (GB).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> ASAI, Toshihiro [JP/JP]; 19-7, Takenodai 1-chome, Nishi-ku, Kobe 651-22 (JP). SWANSON, Brian, L. [US/US]; 11721 Jennifer Court, Concord, OH 44077 (US). TOMKO, Stephen, E. [US/US]; 5131 Eastover Road, Lyndhurst, OH 44124 (US). FERNYHOUGH, Alan [GB/GB]; 29 Misty's Field, Walton-		on-Thames, Surrey KT12 2BG (GB). FRYARS, Michael [GB/GB]; 5 Glenville Court, Silverdale Road, Southampton SO15 2TD (GB).  <b>(74) Agent:</b> ELKINGTON AND FIFE; Prospect House, 8 Pembroke Road, Sevenoaks, Kent TN13 1XR (GB).  <b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> With international search report.
<b>(54) Title:</b> WATER SWELLABLE COMPOSITIONS  <b>(57) Abstract</b>  The invention provides a water-blocking composite comprising a substrate impregnated with or having a coating of a radiation-polymerised water-swellaable composition formed from a hydrophilic monomer and/or oligomer having radiation-polymerisable functionality, and method for production thereof.		

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### WATER SWELLABLE COMPOSITIONS

This invention relates to water swellable materials and radiation cure processes for their preparation. In particular it is concerned with the use of such materials and processes for the preparation of water absorbent or water blocking coatings in a rapid continuous process. A particular application for such materials and processes is in cables to apply water absorbent or blocking coatings to cable components (wires, rods, tubes, strength members, reinforcements etc) in order to block water migration along the cables. Other applications requiring water blocking or absorption can also be amenable to this technology.

Many types of water absorbent or water swellable polymers are known (J. Macromol. Sci. Rev. Macromol. Chem. Phys. C34(4) 1994 pp 607-662). Commercial 'superabsorbent polymers' are available and they have the ability to absorb water or aqueous salt solutions, often in an amount several times their own weight. They are commonly supplied as powders, or as fibres or films. The most common form is powders which are usually incompressible and infusible and so are not ideally suited to application as a direct coating.

Films or fibres may also be prepared in-situ via common coating or spinning techniques which usually involve polymerising hydrophilic monomers in solvents such as water. Similarly they can be applied as coatings to fabrics or other articles by many of the usual water or solvent based coating techniques.

When such coatings or films are prepared in-situ, thermal reaction and/or drying, or removal of water (or other solvent), is required prior to use of such

coatings. In addition they are usually very thin. This makes such known technologies unsuitable for producing a coating which is immediately functional via a rapid low cost continuous process and also unsuitable for producing relatively thick coatings which can exhibit greater swelling behaviour.

US-A-5,204,175 discloses a water absorptive fabric including a layer of a water absorptive polymer whose major components consist of a cross-linked poly (metal salt of acrylic acid) and a water soluble resin.

US-A-5,278,217 discloses a water absorptive composition comprising a thermoplastic elastomer as a first component, a water absorbent resin as a second component, and a third component which consists of a water soluble resin. This composition is suitably used for producing a water absorptive member for protecting optical fibre elements of an optical cable.

US-A-5,179,611 discloses an optical fibre cable comprising of a water absorptive member claimed in US patent 5,278,217.

US-A-4,167,464 and US-A-4,486,489 describe the use of photopolymerisation methods to prepare water absorbent films or fibres from aqueous formulations comprising pre-formed acrylic acid salts as the main component. Since large amounts of water are present in the formulations the speed of the acrylate polymerisation is reduced and this can leave films which are very soft and/or which have a high level of residual tack if the systems are under-cured or not dried by insufficient exposure to the UV radiation and/or post heating. Indeed there may be relatively higher residual unreacted monomers if not fully cured. In addition such films,

after cure, contain relatively high residual water which can be regarded as undesirable per se eg in cables. It can also contribute to a high degree of residual tack and to films being too soft. If drier films are needed from the above formulations, additional heating (drying) is stated as being necessary and this is an obvious inconvenience. The use of high water contents in the formulation can also impair the ability to coat or adhere to some substrates. Such formulations are not well suited to use in rapid continuous radiation coating processes where the coating or film is required to be immediately functional and/or capable of further handling upstream, including passing through dies of tight tolerance, for example in cable production and/or where the presence of water or relatively high levels of water in the cured or uncured composition is undesirable.

Japan unexamined patent application H4-353570 discloses a photopolymerisable resin composition that exhibits excellent anti-fogging, comprising 2-hydroxy ethylacrylate, urethane oligomer and 2-pentylnonyl glucoside. Anti-fogging film is made from this composition by UV radiation.

Japan unexamined patent application H2-149808 discloses a water blocking cable having a central tension member covered with a layer of water absorbent thermoplastic material, whereon loose tube type wave guides are mounted twistedly. The water absorbent thermoplastic comprises polyacrylic acid type.

Japan unexamined patent application H2-162307 discloses a water blocking cable having a non-metallic central tension member covered with a layer of water absorbent thermoplastic material, whereon loose tube type wave guides are mounted, whereon tape of water absorbent

material is wrapped.

Japan unexamined patent application H3-137607 discloses that, to block water migration in a cable with one or plural optical fibre, the outside layer of fibres comprise UV polymerised polymer that swells when exposed to water. Acrylic type, polyethylene oxide UV resin, polyvinyl alcohol type UV resin are preferably used as UV polymerisable resin, but no further details are given.

US-A-5,388,175 discloses an optical waveguide cable with water absorbent powder embedded therein.

The present invention provides a water blocking composite comprising a substrate impregnated with or having a coating of a radiation polymerised water swellable composition.

The invention also provides a method of preparing a water blocking composite, which comprises impregnating or coating a substrate with a composition comprising a hydrophilic monomer and/or oligomer having radiation-polymerisable functionality and exposing the resulting impregnated or coated substrate to radiation to effect curing of the composition.

The invention further provides a radiation curable composition for forming a water blocking composite with a substrate, the composition comprising a hydrophilic monomer and/or oligomer having radiation polymerisable functionality.

The water-swellaable properties of the coating result, in part at least, from the radiation cured monomer(s) and/or oligomer(s). In some cases added water

is not present in the composition and in others some water can be present, as described below, although when present it is preferably at less than 25% by weight of the total initial formulation.

The present invention provides a route to forming water swellable films or coatings in-situ in a rapid on-line continuous process based on radiation curing. The invention makes it possible to coat fibres (eg glass fibres; yarns; optical fibres), wires, or rods (eg cable tension members) or tubes (eg polymeric cable jackets or buffer tubes) or other articles in a rapid continuous process in which no or relatively small amounts of added solvents or water are required. This can, for example, be part of a cabling or jacketing process or part of a rod or fibre making process and be capable of operating at the rapid line speeds commonly used in such processes.

Since there are no large amounts of added solvents or water present there is no special requirement to dry the coatings or films after their formation. As well as thin coatings, relatively thick coatings are also formable. The films or coatings are functional with immediate effect and ready for any subsequent processing stage required in the overall manufacturing process for the end application. Furthermore their characteristics do not change substantially as a result of evaporation of solvent or water on standing or after 'drying'.

In summary, the advantages of our invention include :-

- rapid, convenient, and cost efficient continuous production of a water absorbent or water blocking coating or composite;

- the process is flexible and adaptable to fit in with other stages in a continuous production line (ie

line speeds can be easily varied to accommodate overall production variations) eg it can be part of a cable or wire or fibre or extrusion or pultrusion or UV - pultrusion line;

- the coating is immediately functional and handleable (eg no post-heating or drying);
- the coating contains a relatively low, or zero, amount of water or residual volatile solvent;
- the coating has good wetting on and adhesion to, many surfaces.

In one embodiment, this invention aims to block water migration inside a fibre optic cable. The advantages over other technologies include:

1. Swelling speed (quick swell).
2. Swelling ratio (large expansion).
3. Efficiency and flexibility of the process - fast curing/processing and low cost coating process suitable for on-line, in situ, coating or composite manufacture, without the need for post heating/drying;
4. Coatability on components in a cable.
5. Stability during subsequent cable manufacture operations such as extrusion of upjackets or of the cable jacket.
6. No greases or loose powders are used (such materials can be messy and/or hazardous and are considered inconvenient to use in cabling).

An object of the present invention is to provide a radiation curable composition which after cure can exhibit water absorbing and water swelling properties. A particular object of the invention is to provide a radiation curable composition which after cure, on exposure to water or an aqueous solution can swell with the effect of blocking further ingress of water.



The components of the radiation curable composition may be used within a wide range of relative proportions and comprise:

- one or more hydrophilic monofunctional monomer(s) with radiation polymerisable functionality;
- one or more photoinitiator and/or photosensitiser;

and optionally one or more of the following:

- other monomer or oligomer (not necessarily hydrophilic) with radiation polymerisable functionality;
- crosslinking agent, such as a multi-functional monomer or oligomer, or other additive(s) which may ultimately lead to some crosslinking of the composition;
- hydrophilic or water soluble polymer which is soluble or dispersible in the liquid components of the composition;
- a base;
- an inorganic salt;
- a small amount of water or organic solvent;
- a blowing or foaming agent;
- a surfactant or dispersant;
- adhesion promoter or tackifying resin;
- a fibre or filler.

Other possible additives include coupling agents, air release agents, inhibitors, wetting agents, lubricants or waxes, stabilisers, antioxidants and pigments.

The final compositions of desirable formulations will depend on a number of factors including the required processing speed, coating thickness, water swelling or blocking response in terms of speed and extent, the nature of the surfaces to which the coating is to be applied, and the nature of solutions in which

it is required to function (ie absorb).

The radiation polymerisable hydrophilic mono-functional (with respect to radiation polymerisability) component(s) is preferably selected from groups consisting of:-

- acrylate having mono- or multi- carboxylic acid or sulphonic acid functionality eg acrylic acid or anhydride,  $\beta$ -carboxy ethyl acrylate ( $\beta$ -CEA), maleic or fumaric acid (or anhydrides);

- salts of the acid functional acrylates with sodium, potassium, ammonium as the counter-ion eg sodium acrylate, ammonium acrylate, sodium 2-sulphoethoxy acrylate. Salts of the acid functional acrylates with other bases including organic bases such as amines eg triethylamine, methyl morpholine, hydroxyethyldiethylamine, triethanolamine, hydroxyethyl morpholine, tris(dimethylaminomethyl)phenol. Such salts may be pre-formed or formed in-situ by simple mixing of, for example, acid functional acrylate and base(s);

- acrylate having mono- or multi- hydroxy functional group(s) eg. hydroxy ethyl acrylate (HEA) , hydroxy propyl acrylate (HPA) ; glycerol mono-acrylate; trimethylolpropane mono-acrylate, acrylated epoxides eg Ebecryl 111, acrylated amino alcohols and amino polyols and alkoxylated amines such as those which may be prepared in-situ by simple mixing of, for example, acid functional acrylate and a hydroxyl functional primary amine such as tris(hydroxymethyl)aminomethane;

- acrylamide and its derivatives eg N-hydroxymethylacrylamide, N-tris(hydroxymethyl)methyl acrylamide, other N-alkyl or N-alkoxy substituted acrylamides and acrylamide derivatives such as acrylamidosulphonic acid and its salts;

- ether and polyether acrylates such as monoacrylates having alkoxylated chains eg ethoxy or poly

ethylene oxide structure e.g. polyethylene glycol monoacrylates, polypropylene glycol monoacrylates (eg SR 607 from Sartomer Co), ethoxy ethoxyethyl acrylate (EOEOEA), ethoxylated phenoxy ethyl acrylate, monomethoxy neopentyl glycol propoxylate monoacrylate (Photomer 8127 from Henkel);

- amino-acrylate or amine-acrylate salt, eg N,N-dimethylaminoethyl acrylate (DMAEA); hydrochloride or toluene sulphonate or other salt of DMAEA, which may be formed in situ;

- other monomer and oligomer which are hydrophilic or water soluble eg N-vinyl 2-pyrrolidone, N-vinyl caprolactam, N-vinyl formamide, N-vinyl methyl acetamide, vinyl acetate, tetrahydrofuryl acrylate, acryloxy silane coupling agent, hydrophilic urethane acrylates, hydrophilic epoxy acrylates and hydrophilic polyester acrylates.

In one embodiment the composition preferably comprises mono-functional acrylate(s) as the main component(s). Preferred systems are those incorporating acidic (carboxylic acid, sulphonic acid) functionality, and/or their salts, in the acrylic monomer eg  $\beta$ CEA, with added bases - or those incorporating amine functionality in the acrylic monomer with added acids (eg toluene sulphonic acid or other organic or inorganic acid) as potential counter-ion in a salt or complex - or those systems with high levels of hydroxyl functionality which may be formed in situ.

Particularly preferred systems are based on acid functional acrylates and/or their salts eg  $\beta$ CEA with added base (organic or inorganic base). A little water can aid salt formation but, contrary to the teaching of US 4,486,489, water and/or complete pre-formation (prior to exposure to radiation) of the salt is not essential

for effective swelling or absorption performance.

In practice BCEA is a often preferred acid functional acrylate and preferred to acrylic acid because of its lower hazard. It is less volatile and has a much lower irritancy potential. This makes it more convenient to use in a continuous production line process where the resin formulation is generally not enclosed. In those cases where water or solvent is included in the formulations the % weight levels of the water/solvent are lower with BCEA than would be achieved with a monomer such as acrylic acid. This means a higher proportion (in % weight terms) of the formulation is reactive and this has advantages in terms of lower (or zero) residual unreacted components in the cured film, a faster (less diluted) polymerisation, and less chance of chain transfer or termination reactions.

Acrylate based systems are preferred for the rapid processing requirements but other radical reactive systems which are amenable to radiation initiated polymerisation are also suitable if slower processing speeds can be utilised for the end application. Thus, methacrylate (vinyl ester, eg methacrylic acid, hydroxy ethyl methacrylate, phosphated methacrylate) or vinyl ether - maleate or styrenic or other unsaturated polymerisable systems, eg vinyl sulphonic acid, vinyl phosphonic acid can be used. Addition of acrylate functionality to such systems can be used to speed up their processing.

Cationically polymerisable systems, such as vinyl ether or epoxy functional materials, may also be used in conjunction with, or in place of, acrylate radical polymerisation systems. Cationically polymerisable monomers or oligomers such as vinyl ethers

or epoxy functional materials which are hydrophilic can be used, together with hydroxy functional co-reactants (eg diols or triols). Examples are mono- and multi-vinyl ethers or glycidyl ethers of alcohols, diols and polyols, polyalkylene oxides and epoxidised olefins, cyclic olefins, together with, if desired, polyols and/or epoxy functional materials. Other additives such as those mentioned above and below (polymers, multi-functional analogues, salts etc) can all be included also, although the addition of some free bases may interfere with the cationic polymerisation in some cases.

Other photopolymerisable systems may be also be used such as phenolic photopolymerisations.

In another embodiment a mixture of two largely independent photopolymerising systems may be used eg free radical acrylates plus cationic epoxy - either one or both, but not necessarily both, of which are designed according to the guidelines given to be water swellable. In this way a phase separated radiation cured system based on water swellable polymer particles and/or continuous phase may be produced in-situ.

One or more photoinitiators is preferably selected from the groups below, depending on the type of polymerisation.

For free radical reaction of acrylate by UV radiation or visible light radiation:

- acetophenone type  
e.g. 2-hydroxy-2-methyl-1-phenyl-propan-1-one  
(Darocure 1173)
- acyl phosphine oxide eg Irgacure 1800;
- benzoin type eg benzil dimethyl ketal  
(Irgacure 651);

- benzophenone type;
- thioxanthone type eg isopropylthioxanthone (ITX)
- other sensitiser and co-initiator for UV and visible light curing eg triethanolamine, other amine alcohols, Michler's Ketone, eosin.

For cationic reaction of vinyl ether or epoxy system example photoinitiators are aryl diazonium salts or aryl sulphonium salt eg UV1-6974 and aryl metal complexes such as Ciba CG24-061.

A photoinitiator is not necessary for Electron Beam radiation curing of radical systems.

Other polymerisable monomers or oligomers that can be included can be selected from the above list but are not necessarily hydrophilic and so can also include alkyl acrylates such as iso-octyl acrylate (IOA) and aromatic containing acrylates such as phenoxy ethyl acrylate (PEA). Addition of longer chain acrylates can help the coating to become more flexible.

A small degree of crosslinking is desirable in most cases, though not always essential. Crosslinking can be introduced via multifunctional acrylates and addition of di- or multi- functional acrylate also helps the coating to cure faster. Other interactions can lead to crosslinking and they need not be connected with the polymerisation reaction eg metal-salt formation or complexation interactions or thermal in situ reactions such as OH-COOH condensations in mixtures of hydroxyl and acid functional acrylates. In such mixtures because of heat generated under UV lamps and the heat of polymerisation there is likely to be a small amount of ester formation which effectively is a crosslinking reaction. This small degree of 'adventitious'

crosslinking is sufficient to give improved swelling properties in some mixtures. In others, a crosslinking agent (multifunctional acrylate) can be added.

Crosslinking agents can be compounds having more than one acrylate group. Di- and tri-functional metal acrylates eg calcium or zinc diacrylate or aluminium acrylate and/or di- or multi-valent bases added to acidic monomer containing compositions can also act as crosslinking agents eg calcium hydroxide. Similarly other compounds capable of forming bi- and multi- dentate complexes with any of the functionalities present may act as crosslinking agents

Examples of multifunctional acrylate crosslinking agents include ethylene glycol diacrylate, hexanediol diacrylate (HDDA), tripropylene glycol diacrylate (TPGDA), tetraethyleneglycol diacrylate (TTEGDA), trimethylolpropanetriacrylate (TMPTA), polyethylene oxide diacrylate (PEGDA or Sartomer 344), commercial polyurethane or polyester or polyether acrylates and epoxy acrylates etc.

When multifunctional organic acrylates are added they are usually used at levels of <10% on a molar basis relative to the total polymerisable components. Preferably multifunctional monomers are present at between 5 and 0.05%, on molar basis (of all polymerisable components) and most preferably between 2.0 and 0.1 mol %. These preferred levels are not applicable to other added components which may induce crosslinking such as bases of bi- and tri-valent metals or metal di- and tri-acrylates.

Examples of useful added polymers are those that are water soluble or hydrophilic and are also

soluble or dispersible in the formulations. These include functional and non-functional polymers such as:

- poly(ethylene oxides) such as 'Polyox' and 'Carbowax' (Union Carbide) and other polyalkylene oxides;
- poly(vinylpyrrolidone) (PVP) polymers and copolymers of vinyl pyrrolidone (such as those available from ISP) e.g. Acrylidone,
- poly(vinyl alcohol) and copolymers;
- vinyl acetate polymers and copolymers;
- poly(vinyl ethers) eg poly(vinyl methyl ether) and copolymers of vinyl ethers e.g. Gantrez copolymers from ISP;
- poly(acrylic acid) and copolymers;
- poly(acrylamide) and copolymers;
- polyacrylates such as poly(hydroxymethylmethacrylate) and copolymers;
- copolymers or terpolymers of ethylene or propylene with acrylic acid or acrylic acid esters or vinyl acetate or maleic anhydride and ester or half ester derivatives;
- polymaleic anhydride and copolymers of maleic anhydride and ester or half ester derivatives;
- polyethylene imine and other polyamines including poly(vinyl-pyridine)s and their copolymers;
- starches or celluloses and related structures;
- ionomers.

In a further embodiment an in situ, non-photoinduced, reaction of a hydroxy or acid or other functional radiation polymerisable monomer or oligomer with a suitably functional polymer or small molecule can be used to produce a water swellable system via photopolymerisation. Some examples of the latter (for small molecules) have been mentioned above in the list of preferred radiation polymerisable hydrophilic components. Functional polymers such as, for example, maleic anhydride or acrylic acid copolymers (and/or their



salts or partial salts preformed or prepared in situ with added bases) can be used with, for example, hydroxy functional monomers such as hydroxy ethyl acrylate to produce, by photopolymerisation a water swellable system. Similarly, for example, hydroxy or amine functional polymers such as poly(hydroxy methyl methacrylate) or vinyl alcohol copolymers may be used with acid functional photopolymerisable monomer/oligomer to produce water swellable systems in situ by photopolymerisation. Isocyanate functional polymers, such as isocyanate functionalised polyesters or polyethers, may be used with hydroxy or acid functional acrylates to provide in situ photopolymerisable compositions. In such cases where some reaction between a functional hydrophilic monomer or oligomer and a functional hydrophilic polymer is required then the hydrophilic monomer or oligomer may not necessarily be the major component of the composition.

Examples of bases that can be added include hydroxides, alkoxides, carbonates, carbamates, and hydrogen carbonates, di- and tri- basic phosphates or citrates, - of ammonium and of Group I and II metals including sodium, potassium, magnesium, and calcium. Organic bases such as amines eg triethanolamine or triethylamine (TEA) or morpholines (eg N-methylmorpholine, MeM) or piperidines or tris(dimethylaminomethyl)phenol can also be used. In the absence of pre-dissolving in water or other diluent, the bases that are solid are used as powders, dispersed in the liquid components of the formulation. Bases are usually added to compositions containing acid functional acrylates.

Examples of added salts that may be used include halides, acetates, sulphates, carboxylated and

phosphates of metals and ammonium or other amine/substituted ammonium counter-ions.

Examples of solvents which may be added include alcohols, glycols polyols, ethers and alkoxyated solvents. Examples include ethanol, methanol, isopropanol, ethylene glycol, propylene glycol, polyalkylene oxides, glycerol, trimethylolpropane, alkoxyated derivatives and ethers of the above (e.g. Photonols from Henkel). Levels of added solvents, if used, are preferably lower than 25% by weight of the total composition.

Addition of surfactant up to 40% of the total composition weight can increase swell response. Example surfactants which can be used with or without water can be non-ionic, eg alkoxyated amines, alcohols, esters, oils, fatty acids, nonylphenol and ethanolamides and sorbitan esters, alkyl aryl polyether alcohols eg Triton X100 (from Rohm & Haas), or anionic or cationic, or amphoteric. Surfactants can help to stabilise same systems with dispersed salt or base or other undissolved solid.

Addition of a blowing agent which can generate gas when contacted with water or on heating (eg during exposure to UV lamp and/or consequential heat of polymerisation reaction or other application source of heat) can increase the swell response in some cases.

Examples are sodium bicarbonate, sodium carbonate, ammonium carbonate, ammonium bicarbonate with or without organic or inorganic acid (eg acetic acid, citric acid, oxalic acid, tartaric acid or keto-acid, or hydroxy acids such as lactic acid, etc), or  $\text{NaAl}(\text{SO}_4)_2$ ,  $\text{KAl}(\text{SO}_4)_2$ ,  $\text{NaH}_2\text{PO}_4$  or  $\text{NaBH}_4$ ; or  $\text{C}_6\text{N}_6$ ,  $\text{BaN}_6$ , azo compounds

such as azodicarbonamide etc. It will be seen that some such as of those blowing agents such as carbonates, hydrogen carbonates and some phosphate derivatives may usefully act both as blowing agent and base in certain formulations. Here the avoidance of excessive heat build up at the mixing stage (eg gradual addition) is required to avoid premature activation of the blowing agent effect in such systems. Certain stabilising additives such as ketones may be added to improve stability and pot-life in some of these systems, as illustrated by comparing examples 7.1, 7.2 and 7.3.

Foamed structures can be produced by simple use of hydroxide bases such as sodium hydroxide, although the mechanism of foam formation is not clear.

Addition of fillers such as inorganic particles (eg fumed silica, mica) or polymer powders or fibres e.g. polyethylene powder may increase swelling response in certain systems.

Addition of hydrophilic fibre, water soluble fibre or hydrophilic surface treated fibre can help to increase swell response in certain formulations. Examples include ground cellulosic fibres, polyvinyl alcohol fibre.

Addition of oligomer with radiation polymerisation functionality and phosphoric acid/ester helps to increase adherability to certain substrates. Examples are phosphoric acid diacrylate, hydroxymethyl-methacrylate-phosphate and styrene phosphonic acid.

A simple coating process can comprise:

- UV radiation or other radiation curing equipment

- coating die unit.

The composition used in the invention has a suitable range of viscosity to be coated at suitable thickness on cable component materials such as central tension member, wave guide, tape, fibre reinforcement, etc. by means of common coating methods such as roll coater, bath dipping, coating die, syringe, extrusion coating die, which is placed together with radiation curing equipment. This coating process can be part of a continuous cable manufacturing line.

The composition can be polymerized by radiation such as UV radiation or visible light at suitable curing speed that can meet economical production speed of cable manufacturing. Since the composition does not always need to be heated for coating and curing a cooling stage is not required. Thus, the coating and UV or light curing system is relatively convenient, compact and easy handling and of low expense. Furthermore, since this composition is quick curing by radiation, the coating/curing system can be synchronized to cable manufacturing condition variations and this leads to low maintenance benefit and high productivity.

The compositions can be coated and cured on cable components (wave guide, tension member, buffer tubes, wrappings, tapes etc.) at a range of thickness of 0.001" up to 0.2". The compositions can have a range of swell response time from in seconds to minutes after it comes into contact with water. This coating (cured composition) can swell, for example, at a range of 2 or more over original thickness. These benefits give the cable design flexibility to minimize the space in the cable where water can migrate and need to be filled with other water blocking materials such as tape, powder etc.

This leads to a water proof cable system with less cost, easy installation and maintenance (no grease, no powder).

The coating and radiation curing system can be built either within or in the cable manufacturing line or off line. A typical system is illustrated in Fig. 1. This system consists of a reservoir having coating die and a tank of radiation curing composition and a pump unit and UV radiation unit(s) and control unit. The UV radiation unit can for example, use one or more UV lamps of 100 to 800 WATT per inch energy depending on cure condition required by cable production speed and coating condition. The cable component(s) are/is coated and covered with the radiation curable component then passed to the cable assembly unit. Alternatively, the coated components can be stored and used at a later date for cable assembly.

### **Examples**

Tests used to characterise materials include observation of viscosity (for suitability to coat) and of viscosity stability over time (ie pot-life), observation of swelling response in water, measurement of time to block water progress along a coated rod, tackiness and degree of cure or relative cure speed, adhesion to substrates,

In practical applications it will be recognised that there will be a balance between various factors (eg viscosity and required coating thickness, swell response, cure speed, adhesion to substrate, tackiness of coating) which will dictate which formulations are most appropriate. All the examples given exhibit useful viscosity and cure speeds for most envisaged applications and most exhibit suitably long pot-lives.

#### **1. Swellability of films**

### Film Preparation

A composition as described is coated on to a glass microscope slide using a 'wire-wound rod metering apparatus' e.g. K-bar No 9 (quoted wet film thickness of 125 microns) and the coated slide was then placed on to a supporting baseplate (on a conveyor belt) which is then exposed to UV via a conveyor. The lamp used was a Fusion F600 with a D bulb. The distance from the bottom of the lamp unit to the base plate was 57mm. A conveyor speed of 6-7m/min was used. Unless otherwise stated, two passes were made.

### Testing

The coated slides are immersed in water and observed for the appearance of swelling behaviour in terms of how quickly is there a response and how large is the response.

### Example formulations

All ratios in the Tables are molar except where stated otherwise.

All the formulations in the Tables contain 3wt % (based on polymerisable materials) Irgacure 651 as photoinitiator. All these coatings exhibited significant visible swelling in less than 1 hour of immersion in water. Some responded in minutes and some in less than 1 minute.

Table 1 gives examples of formulations incorporating hydroxyl or amine or carboxylic acid or other mono-functional hydrophilic acrylates with and without added multifunctional acrylate (TTEGDA).

Table 1

Ex No	$\beta$ CEA	HEA	HPA	EOEOEA	DMAEA	TTEGDA
1.1	1.0	1.0				
1.2	1.0		1.0			
1.3	1.0	1.0		0.25		
1.4	1.0	1.0			0.33	
1.5	1.0	2.0				
1.6	2.0	1.0				
1.7	2.0	1.0	1.0			
1.8	1.0		1.0			
1.9	1.0	1.0				0.002
1.10	1.0					0.002
1.11	1.0				0.75	0.002
1.12		1.0				0.002

Table 2 gives examples of non-aqueous formulations with added inorganic bases or salts, which show significant swelling in less than 1 hour immersion in water. Many show significant swelling in under 5 minutes and some in under 1 minute. The inorganic materials are usually powdered and dispersed in the liquid components prior to UV cure.

<u>Ex No</u>	$\beta$ CEA	HEA	NaAc	NaOH	Na <sub>2</sub> CO <sub>3</sub>	NaHCO <sub>3</sub>	NH <sub>4</sub> Ac	TTEGDA
2.1	1.0	1.0		0.8				
2.2	1.0	1.0				0.8		
2.3	1.0	1.0			0.4			
2.4	1.0	1.0	0.8					
2.5	1.0	1.0		0.8				0.002
2.6	1.0					0.75		0.002
2.7	1.0						0.75	0.002

Table 2 (contd)

<u>Ex No</u>	$\beta$ CEA	PEA	PEG 2000	TTEGDA	Na <sub>2</sub> CO <sub>3</sub>	NaHCO <sub>3</sub>	NaOEt	NH <sub>4</sub> HCO <sub>3</sub>
2.8	1.0	0.3		0.002				0.95
2.9	1.0		0.03	0.002				0.95
2.10	1.0	0.3		0.002		0.95		
2.11	1.0		0.03	0.002		0.95		
	1.0		0.03	0.002			0.48	
2.13	1.0		0.03	0.002				
2.14	1.0	0.3		0.002	0.48			
2.15	1.0		0.03	0.002	0.48			



Table 2 (contd)

Ex No	BCEA	TTEGDA	$(\text{NH}_4)_2\text{HPO}_4$	$\text{NaNH}_4(\text{HPO}_4)$	$\text{Na}_3\text{PO}_4$ (anhydr)	$\text{Na}_2\text{HPO}_4$	$\text{Na}_3\text{PO}_4$
2.16	1.0	0.002	0.75				
2.17	1.0	0.002		0.75			
2.18	1.0	0.002			0.58		
2.19	1.0	0.002				0.62	
2.20	1.0	0.002					0.65

Table 2 (contd)

Ex No	BCEA	PEA	TMPTA	PEGDA	$\text{Na}_2\text{HPO}_4$
2.21	1.0	0.3	0.002		0.6
2.22	1.0	0.3		0.002	0.6

Table 2 (contd)

Ex No	BCEA	HBA	TTEGDA	$\text{KOCH}_3$
2.23	1.0		0.002	0.6
2.24	1.0	0.5	0.002	0.6

(HBA=hydroxybutyl acrylate)

Table 3 gives examples of formulations incorporating added inorganic bases/salts with small amounts of water (<25 weight % of the total formulation). In these compositions the base is dissolved or dispersed in water and then added slowly to the stirring mixture of other components.

Ex No	$\beta$ CEA	HEA	EOEOEA	NaOH	$\text{Na}_2\text{CO}_3$	$\text{NH}_4\text{OH}$ aq <sup>(1)</sup>	WATER (%wt)	TTEGDA
3.1	1.0	1.0		0.75			17.2	0.002
3.2	1.0	1.0			0.75		15.1	
3.3	1.0	1.0			0.75		15.1	0.002
3.4	1.0	1.0			0.375		16.8	0.002
3.5	1.0		1.0		0.375		13.9	0.002
3.6	1.0	1.0				0.75	17.4*	0.002
3.7	1.0	1.0				0.75	5.6**	
3.8	1.0					0.75	9.0**	0.002
3.9	1.0					0.6	7.6**	0.002
3.10	1.0					0.75	20.2	0.002

(<sup>1</sup>) Ammonium hydroxide (ACS reagent from Aldrich Chemical Co) was used (and supplied) as a solution in water with an approximate water content of 40% by weight (approx 60% ammonium hydroxide, equivalent to about 29% ammonia).

\* Includes water content from aqueous ammonium hydroxide solution.

\*\* The stated water content is that which is already present in the ammonium hydroxide solution ie no extra water is added.

Table 4 gives examples of formulations with added organic bases; (all contain 0.002 moles TTEGDA per 1.0 mole BCEA).

Ex No	BCEA	PEA	IOA	PEG 2000	PEG 400	TEA	MeM
4.1	1.0			0.03		0.75	
4.2	1.0	0.29				0.75	
4.3	1.0				0.14	0.75	
4.4	1.0		0.3			0.75	
4.5	1.0						0.75
4.6	1.0			0.03			0.75
4.7	1.0	0.29					0.75
4.8	1.0		0.3				0.75

Table 4 (cont.)

Ex No	BCEA	PEA	IOA	Meth- anol	TEA	MeM	(NH <sub>4</sub> ) <sub>3</sub> Citrate	(CH <sub>3</sub> ) <sub>4</sub> - NOH
4.9	1.0			20wt%	0.75			
4.10	1.0	0.3			0.75			
4.11	1.0		0.3			0.75		
4.12	1.0	0.3				0.75		
4.13	1.0		0.3		0.75			
4.14	1.0						0.3	
4.15	1.0							0.4

Table 5 gives examples with added polymers:

Ex No	BCEA	HEA	NaOHaq *	NH <sub>4</sub> OHaq **	NaAc	TTEGDA	PVP
5.1	1.0	1.0			0.8		15wt%
5.2	1.0	1.0		0.8			15wt%
5.3	1.0	0.25	0.75				15wt%
5.4	1.0		0.75			0.002	15wt%

\* Water content = 19.3 wt% for 5.3 and 22.2 wt% for 5.4

\*\* Water content = 5.0 wt%

Table 5 (cont.)

Ex No	BCEA	NH <sub>4</sub> OH	TTEGDA	PVP	Ethyl cellulose	Methyl cellulose
5.5	1.0	0.95	0.002			3wt%
5.6	1.0	0.95	0.002		5wt%	
5.7	1.0	0.95	0.002	10wt%		

## 2. Water Blocking Ability of Coated Rods

Glass reinforced composite rods were coated with the composition by the following method:

A length of rod (eg at least 150 mm, usually 1m) is wetted with the resin formulation and pulled through a die or tube of fixed diameter and then exposed to UV radiation (Fusion F600 lamp with D bulb). The coated rod is then placed inside a transparent tube (glass; at least same length as coated rod). Usually (unless otherwise stated) the coated rod diameter was about 2.5mm and the glass tube's internal diameter was 3.4mm or 4mm.

This combination of coated rod and glass tube was then attached, by suitable rubber tubing, to a reservoir of water (eg as in Figure 2). At the appropriate moment the water is released from the reservoir and the time ('blocking time') for the progression of water down the coated rod to cease (as a result of the swelling behaviour of the coating) is recorded.

Table 6 shows examples of some of the above formulations, and of some of the Table 7 examples, tested in a water blocking test on coated rods.

Table 6

<u>Ex</u> <u>No</u>	Blocking time/s	<u>Ex</u> <u>No</u>	Blocking time/s	<u>Ex</u> <u>No</u>	Blocking time/s	<u>Ex</u> <u>No</u>	Blockin g time/s
4.14	100	2.1	180	3.4	150	5.3	120
4.13	120	2.2	150	3.6	210	5.4	210
4.12	160	2.7	150	3.7	150	5.5	57
4.11	100	2.16	80	3.9	27	5.6	70
4.10	33	2.17	50	3.10	60	5.7	25
4.9	145	2.19	35				
		2.20	95			7.4	45
		2.23	55			7.7	45
		2.24	50			7.8	108
						7.15	30

In an adaptation of the above water blocking experiment, the same test procedure was carried out on glass fibre reinforced composite rod specimens whereby the polymer matrix of the composite was composed of the water swellable formulation (examples 7.7, 7.8).

The specimens of examples 7.7 and 7.8 were made using a UV pultrusion process which involves impregnating continuous glass fibres in a resin bath containing the formulation, passing the wetted fibres through a die (1.8mm diameter) and UV curing to produce a cured composite with an approximate fibre content of around 28wt%. The glass fibre reinforced rods were inserted into 4mm (internal diameter) glass tubes and evaluated in tube blocking tests as detailed above.

Table 7: Miscellaneous examples illustrating formulation stabilisation (1/2/3); exceptionally low tack or tack free systems (4/5/6); rod composites with water swellable matrix (7/8); use of surfactants (9/10/11/12); non-hydrophilic crosslinking agents (13/14); inert inorganic additives (15):-

Ex No	7.1 <sup>(1)</sup>	7.2 <sup>(2)</sup>	7.3 <sup>(3)</sup>	7.4	7.5	7.6	7.7	7.8
BCEA	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Ammonium Carbamate	0.4	0.4	0.4					
NH <sub>4</sub> HCO <sub>3</sub>								0.8
NH <sub>4</sub> OH				0.95			0.95	
KOH					0.6	0.6		
TTEGDA	0.002	0.002	0.002	0.002				
TPGDA					0.002	0.002	0.002	0.002
Pentanone		4wt%	4wt%					
Butanone								4wt%
BYK A555								0.5%
PVP				10wt%			5wt%	
Zinc acrylate					10wt %			
Ca(OH) <sub>2</sub>						8wt%		
Time to** swell (s)		51	40	75	60	150		

\*\* water immersion of cured film on glass slide.

(1) UV cure not possible due to short pot life (<15min.).

(2) specimen cured 1 hour after mixing.

(3) specimen cured 24 hours after mixing.

Table 7 (cont.)

Ex No	7.9	7.10	7.11	7.12	7.13	7.14	7.15
BCEA	1.0	1.0	1.0	1.0	1.0	1.0	1.0
NaOH	0.8	0.8	0.8	0.8			
NH <sub>4</sub> OH					0.8		0.95
NH <sub>4</sub> HCO <sub>3</sub>						0.8	
TPGDA	0.002	0.002	0.002	0.002			
TTEGDA							0.002
HDDA					0.002		
CN104 <sup>(1)</sup>						0.002	
Butanone						4wt%	
BYK A555 <sup>(2)</sup>						0.5wt%	
Ethylan TU <sup>(3)</sup>		7.5wt%					
TEOAO <sup>(4)</sup>			7.5wt%				
Aerosol OT <sup>(5)</sup>				7.5wt %			
Cabosil M5 <sup>(6)</sup>							1wt%
Time to** swell (s)	95	75	130	165	180	40	

\*\* water immersion of cured film on glass slide.

(1) Epoxy acrylate oligomer (Sartomer)

(2) air release additive (BYK Chemie)

(3) non-ionic surfactant (Akcros)

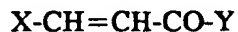


- (4) triethanolamine oleate
- (5) dioctyl sodium sulfosuccinate
- (6) fumed silica (Cabot)

**CLAIMS:**

1. A water-blocking composite comprising a substrate impregnated with or having a coating of a radiation-polymerised water-swellaable composition formed from a hydrophilic monomer and/or oligomer having radiation-polymerisable functionality.
2. A composite according to claim 1, in which the substrate is a component of a cable.
3. A composite according to claim 1 or 2, in which the substrate is a continuous fibre.
4. A composite according to any of claims 1 to 3, in which the composition constitutes a coating on the substrate.
5. A method of preparing a water-blocking composite, which comprises impregnating or coating a substrate with a composition comprising a hydrophilic monomer and/or oligomer having radiation-polymerisable functionality; and exposing the resulting impregnated or coated substrate to radiation to effect curing of the composition.
6. A method according to claim 5, in which the substrate is a component of a cable, e.g. strength member, buffer tube, wrapping or tape or ribbon.
7. A method according to claim 5 or 6, in which the substrate is a continuous fibre (filaments, tow, yarn, ribbon, mat or tape) or a metal, plastic or fibre reinforced plastic rod, wire, sheet or other shape.

8. A method according to any of claims 5 to 7, in which the substrate is coated with the composition.
9. A method according to any of claims 5 to 8, in which the composition also contains one or more photoinitiator and/or photosensitiser suitable to promote polymerisation of the monomer or oligomer.
10. A method according to any of claims 5 to 9, in which the radiation is UV radiation.
11. A method according to any of claims 5 to 10, in which the composition is substantially water-free.
12. A method according to any of claims 5 to 10, in which the composition contains less than 25%, preferably less than 20%, more preferably less than 15%, and most preferably less than 10%, by weight of water.
13. A method according to any of claims 5 to 12, in which the composition also contains a crosslinking agent having two or more radiation-polymerisable groups, or in which the monomer or oligomer has self-crosslinking capability.
14. A method according to any of claims 5 to 13, in which the hydrophilic monomer is of the general formula:



in which

X is -H or -COOH;

Y is -OH, -OR<sup>1</sup> or -NHR<sup>2</sup>;

$R^1$  is  $C_1$ - $C_4$  alkyl substituted by -OH,

-COOH, -SO<sub>3</sub>H, -OR<sup>3</sup>, -NR<sup>3</sup><sub>2</sub>

where  $R^3$  is  $C_1$ - $C_4$  alkyl or  $R^1$  is a

polyalkylene oxide chain terminated by

an alkyl group or OH or COOH or amine,

or a poly(carbonylalkylene

oxide) chain terminated by an -OH group

or COOH group;

$R^2$  is  $C_1$ - $C_4$  alkyl substituted

by -SO<sub>3</sub>H, -OH, and/or -COOH,

or a salt thereof.

15. A method according to claim 14, in which the salt is an alkali metal, ammonium or hydrocarbylammonium salt of a carboxylic acid or sulphonic acid group, or a hydrochloride or organic, e.g. toluene, sulphonate salt of an amine group.

16. A method according to any of claims 5 to 13, in which the hydrophilic monomer or oligomer is selected from N-vinyl pyrrolidone, N-vinyl caprolactam, vinyl acetate, tetrahydrofuryl acrylate, acryloxy silane coupling agent, hydrophilic urethane acrylate, polyester acrylate, polyether acrylate, and hydrophilic methacrylates.

17. A method according to any of claims 5 to 13, in which the hydrophilic monomer is selected from monofunctional vinyl ethers and/or glycidyl ethers of aliphatic or cycloaliphatic alcohols, diols or polyols with 20 or less carbon atoms (in the alcohol, diol or polyol), and/or monofunctional vinyl ethers or glycidyl ethers of polyalkylene oxides, and/or mono-epoxidised olefins with 20 or less carbon atoms.

18. A radiation-curable composition for forming a water-blocking composite with a substrate, the composition comprising a hydrophilic monomer and/or oligomer having radiation-polymerisable functionality.

19. A composition according to claim 18, which also contains one or more photoinitiator(s)/photosensitiser(s).

20. A cable containing a water-blocking composite according to any of claims 1 to 4.

21. Use of a composition according to claim 18 or 19 for forming a water-blocking composite with a substrate.

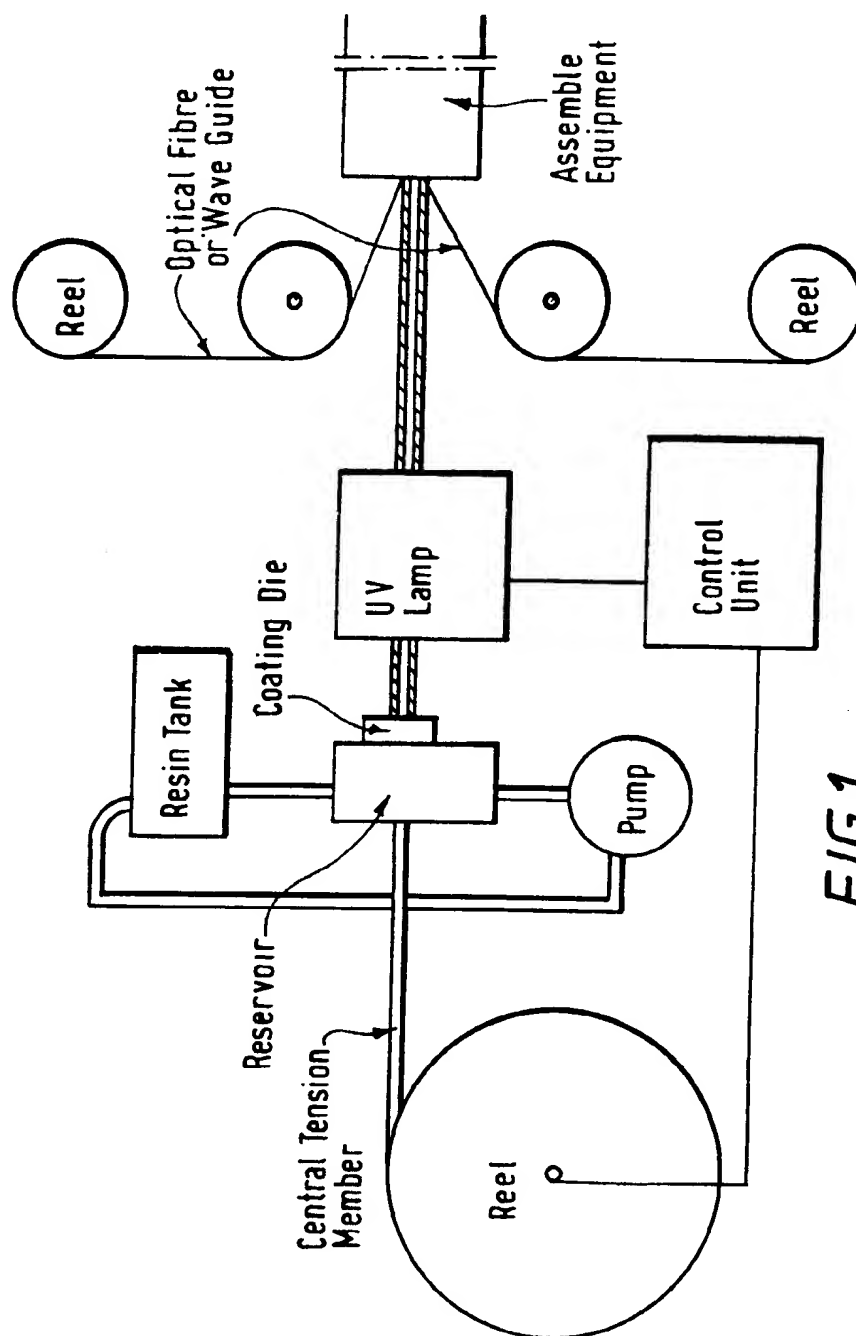
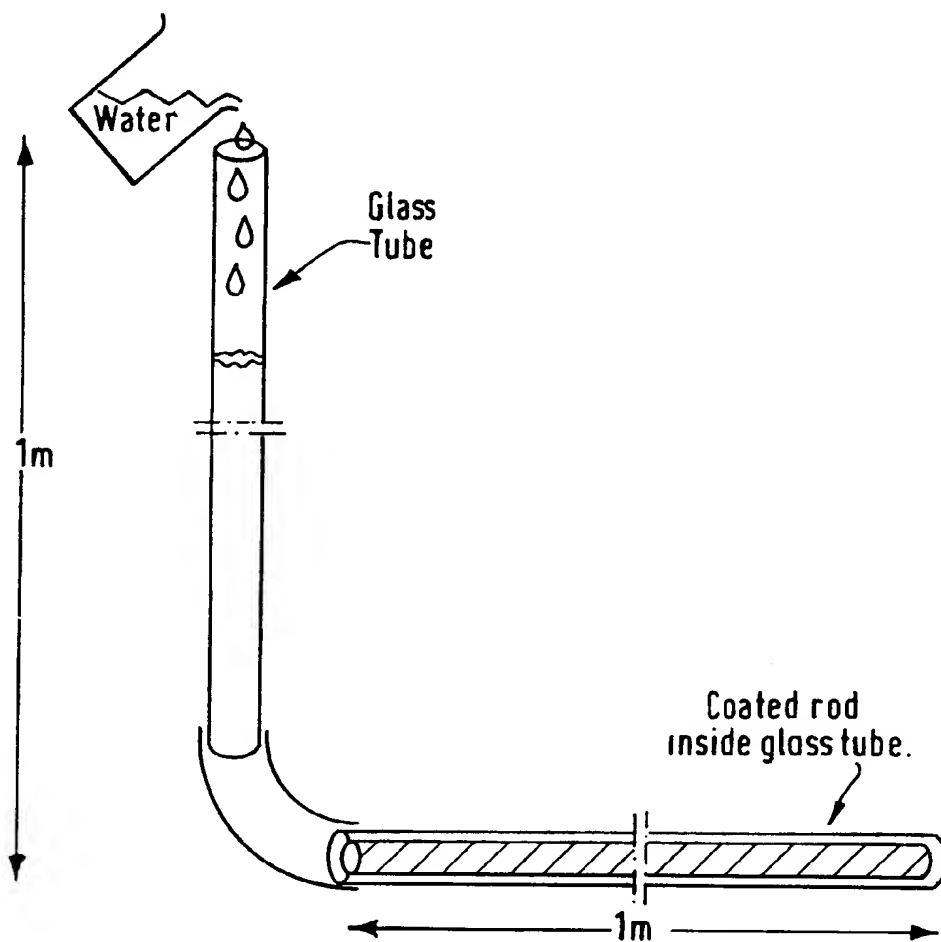


FIG. 1.

*FIG. 2.*

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 96/01244

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 H01B7/28 G02B6/44

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H01B G02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE WPI Section Ch, Week 9105 Derwent Publications Ltd., London, GB; Class A97, AN 91-032129 XP002010607 &amp; JP,A,02 300 360 (DYNIC CORP) , 12 December 1990 see abstract</p> <p>---</p>	<p>1,3-5,7, 8,10, 14-18,21</p>
X	<p>DATABASE WPI Section Ch, Week 9019 Derwent Publications Ltd., London, GB; Class A96, AN 90-144362 XP002011102 &amp; JP,A,02 091 129 (NIPPON SHOKUBAI KAGAKU) , 30 March 1990 see abstract</p> <p>---</p>	<p>1,3-10, 14-19,21</p>
	<p>--- -/--</p>	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

20 August 1996

Date of mailing of the international search report

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 96/01244

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 014, no. 034 (C-679), 23 January 1990 & JP,A,01 271434 (NIPPON SHOKUBAI KAGAKU KOGYO CO LTD), 30 October 1989, see abstract ---	1,3-5, 7-12, 14-19,21
A	EP,A,0 353 775 (MITSUBISHI PETROCHEMICAL) 7 February 1990 see the whole document -----	1-21

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 96/01244

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-353775	07-02-90	JP-A- 2044305	14-02-90
		JP-A- 2068816	08-03-90
		JP-A- 2068817	08-03-90
		JP-A- 2068818	08-03-90
		JP-A- 2068819	08-03-90
		US-A- 5071221	10-12-91
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